Reactions of $PhIX_2$ I(III) oxidants with heavy triphenyl pnictines

*Sathsara Egalahewa, Antonino Aprile, and Jason L. Dutton**

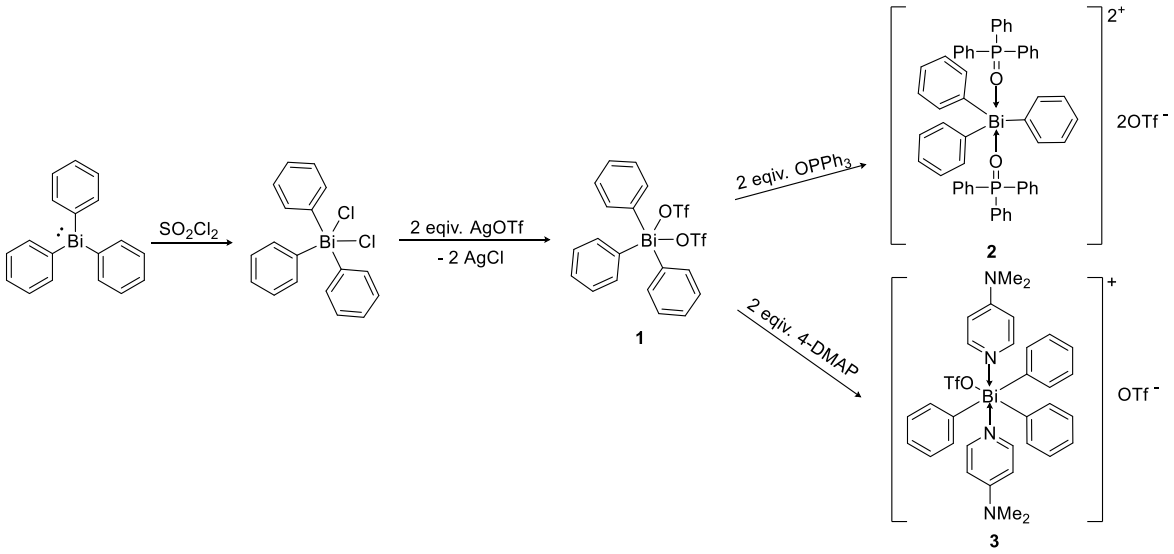
Department of Chemistry and Physics, La Trobe Institute for Molecular Science, La Trobe University, Melbourne, Victoria, Australia, 3086

ABSTRACT

The reactions of $[PhI(pyridine)_2]^{2+}$, $PhI(OAc)_2$ and PhI(OTf)(OAc) with Ph_3As, Ph_3Sb and Ph_3Bi are described. The reactions of $[PhI(pyridine)_2]^{2+}$ with Ph_3Sb and Ph_3Bi affords dicationic Pn(V) complexes ligated by pyridine in one step. These were previously reported by Burford in multi-step syntheses. Reactions with $PhI(OAc)_2$, which were already known for Sb and Bi giving Pn(V) diacetates, were confirmed to give the same type of compound for As. Reactions with PhI(OAc)(OTf) were less selective, resulting in the isolation of iodonium cations $[Ph\text{-}I\text{-}Ph]^+$ for As and Bi, while Ph_3Sb gave an oxobridged di-antimony species characteristic of the decomposition of a high valent triflate bound species.

Introduction

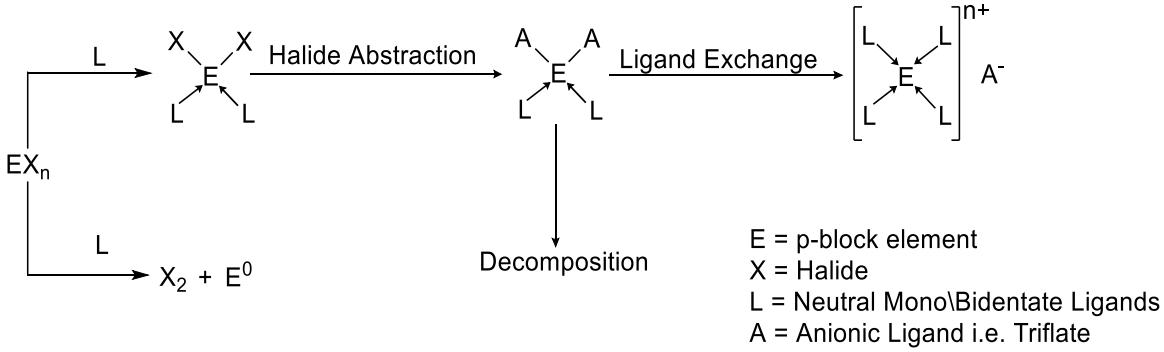
The synthesis of polycationic species of the heavier late p-block elements has seen little investigation as compared to the lighter elements due to reactivity of the intermediates and target complexes as well as the requirement of a main-group halide starting material which can be difficult to handle.[1] Much of the work utilises halide abstraction resulting in triflate containing species which can be used in further ligand exchange with other mono-, di- and tridentate ligands.[2] Work by Burford *et al.* highlights this as using the above method they were able to isolate the bis-triflate bismuth(V) compound **1** followed by exchange with pyridine ligands to give the dicationic bismuth species **2** and monocationic species **3** (Scheme 1).[3] The corresponding chemistry for antimony was also reported by the Burford group.[4]



Scheme 1. Isolation of bismuth(V) complexes **2** and **3** using triphenylbismuth.

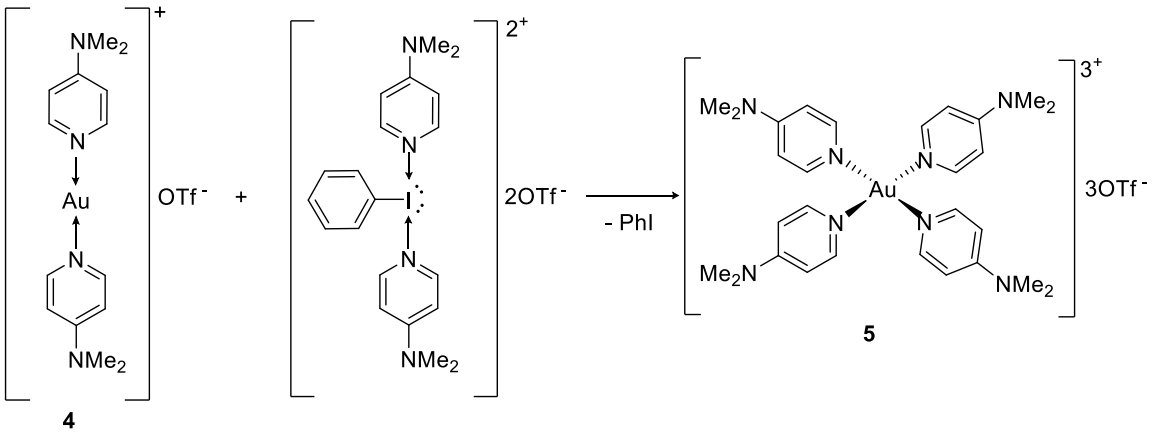
This strategy is a general route to ligand stabilized polycations in groups 15 and 16. As shown in Scheme 2, the commonly used route in the literature is the abstraction of a halide with a species

that introduces triflate or another good leaving group, with some examples requiring a specific halide for this reaction to proceed as well as the element in the correct oxidation state.[5] Addition of ligands to late main group halides can result in spontaneous reduction reactions, with elimination of elemental halogen as a possible by-product leading to deleterious effects.[6] The triflate adducts can be very sensitive to moisture and air making them relatively difficult to store and handle.



Scheme 2. The common method utilised for the isolation of cationic p-block species showing possible undesired outcomes.

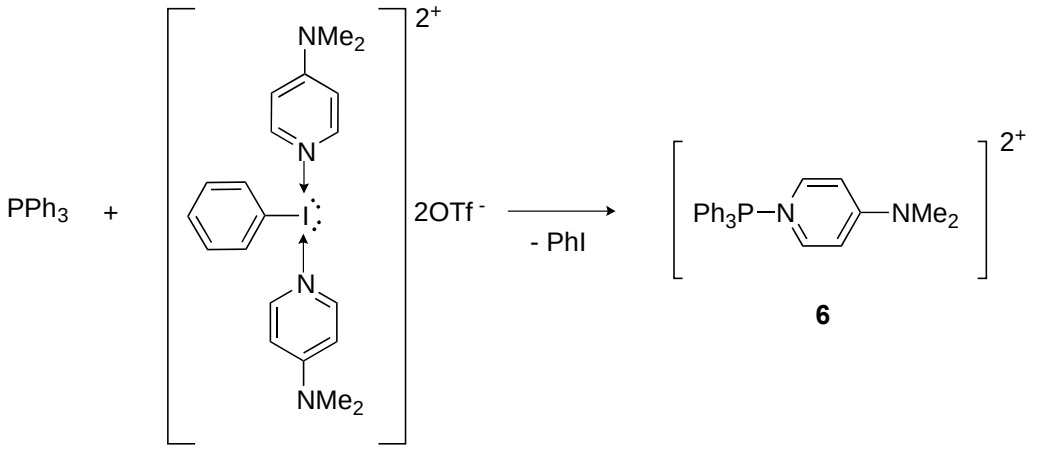
The issues of intermediate stability and the side reactions that can occur during the isolation of these molecules make a more direct route potentially attractive. Our group has been examining the chemistry of dicationic I(III) reagents $[PhI(Pyr)_2]^{2+}$ (Pyr = Pyridine, 4-DMAP, 4-Cyanopyridine) with a major feature of their chemistry being of simultaneous oxidation of a metal along with delivery of the pyridine ligands. An example is the generation of Au(III) trications **5** from Au(I) precursor **4** (Scheme 3).[7]



Scheme 3. Isolation of cationic gold species **5** via oxidation with $[PhI(Pyr)_2]^{2+}$ oxidants.

These I(III) pyridyl compounds were first reported in 1994 by Weiss and later reinvestigated by Zhdankin.[8-10] Ritter also used the oxidant to access pyridine stabilized Pd(IV) complexes, where the pyridine could be displaced with ^{18}F labelled fluoride to generate PET labelling agents.[11] Wengryniuk has recently shown the efficacy of these oxidants in oxidative ring formation reactions.[12-14]

In the main group we have explored the chemistry of these dicationic I(III) oxidants with aromatic group 16 rings, which largely resulted in electrophilic aromatic substitution type reactions on the ring or ring substitutents.[15, 16] We also reported one reaction in group 15, the reaction of Ph_3P with $[PhI(4\text{-}DMAP)_2]^{2+}$, which resulted in oxidation of phosphorus to P(V) and ligation of a 4-DMAP giving dicationic complex **6** (Scheme 4),[17] previously reported by Burford using the oxidation/halide abstraction method from the phosphine.[18] No reaction is observed between PPh_3 and $PhI(OAc)_2$. For PhI(OAc)(OTf) oxidation occurs giving a proposed P(V) triflate ligated intermediate which rapidly decomposes to $Ph_3P{=}O$ and triflic anhydride.



Scheme 4. Oxidation and delivery of 4-DMAP ligand to triphenylphoshpine giving dication **6**.

We initially viewed these reactions as indicating that I(III) oxidants are incompatible with phosphine ligands, although have since found in some cases they are compatible when the phosphine is bound to a metal.[19] In light of Burford's work on heavier pnictogen(V) dications described above, we wondered if these I(III) dications could be an effective reagent for their generation, circumventing the steps involving halogenation/halide abstraction.

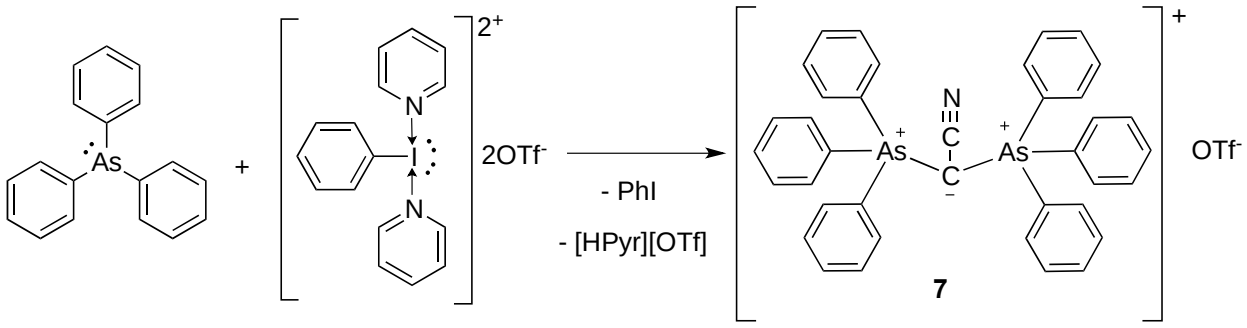
In this study we examined the ability of iodine(III) oxidants with anionic and neutral ligands as potential reagents to isolate dicationic complexes of arsenic, antimony and bismuth using $AsPh_3$, $SbPh_3$ and $BiPh_3$ as starting materials.

Results and Discussion

Arsenic

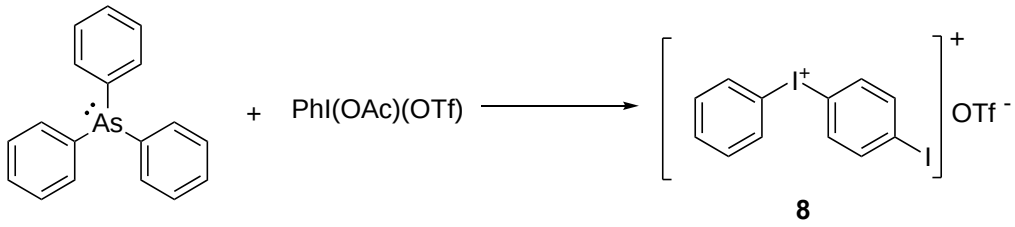
Triphenylarsine was stirred with 1 equivalent of $[PhI(Pyr)_2][OTf]_2$ in CD_3CN for 4 hours resulting in a colourless solution. Acetonitrile was employed as reactions in $CDCl_3$ or CD_2Cl_2 resulted in the immediate formation of complex mixtures. The ^1H NMR spectrum of the *in situ* CD_3CN

reaction had peaks corresponding to PhI indicating that an oxidation has occurred, at least one other phenyl containing species and protonated pyridine as compared with an authentic sample. A colourless single crystal was grown from the solution left to stand at -30°C for 24 hours. X-ray crystallography revealed the product to be bis-As(V) cation (**7)** with a completely depronotated acetonitrile fragment bridging the two As(V) centres. This compound has been reported via a different route.[20] We surmise in this case that acetonitrile coordinates to the oxidized arsenic centres, rendering the hydrogen atoms more acidic, resulting in deprotonation by pyridine and eventual rearrangement to the observed product. It should be noted here that the As analogue of **3** is not known and may not be stable as it is for Bi and Sb.



Scheme 5. Oxidation of Ph_3As using $[PhI(Pyr)_2][OTf]_2$ giving **7**.

The addition of 1 equivalent of PhI(OAc)(OTf) to triphenylarsine in $CDCl_3$ resulted in an immediate change in ^1H NMR with all starting material consumed within minutes and the formation of a complex mixture. A vapor diffusion of the solution with n-hexane led to colourless crystals. X-ray crystallography of a single crystal revealed a diaryliodonium triflate salt (**8**) via unit cell analysis (Scheme 6),[21] this cation was also observed in the mass spectrum of the reaction mixture. No oxidized arsenic species could be identified in the mass spectrum. Compound **8** is known and most commonly synthesized by the reaction of iodoarenes with a suitable oxidant.[22]



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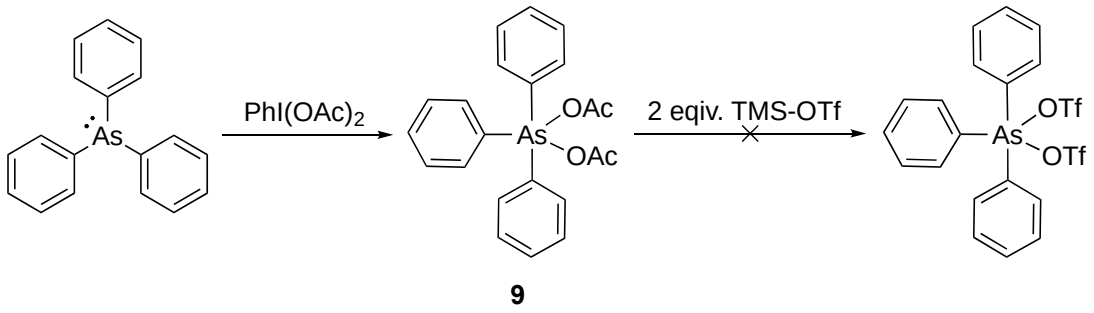
Scheme 6. Addition of PhI(OAc)(OTf) to Ph_3As results in isolation of **8**. The fate of the As could not be determined.

Next, triphenylarsine was reacted with $PhI(OAc)_2$ in $CDCl_3$. The ^1H NMR spectrum of the colourless reaction mixture confirmed that reaction was driven to completion with no starting material after stirring for 24 hours. The spectrum had peaks corresponding to PhI and another species which indicates the possible formation of As(V) as the iodine became reduced. Colourless crystals were grown at -30°C. The crystals were of poor quality, but X-ray crystallography allowed for structural confirmation of the formation of triphenylarsine diacetate (**9,** Scheme 7). Compound **9** is a known compound and has been synthesized by other routes.[23]

Attempts to exchange the acetate groups in **9** for triflates as a better leaving group using TMS-OTf resulted in no reaction. In summary, reactions of these I(III) oxidants with triphenylarsine did not result in productive advances.

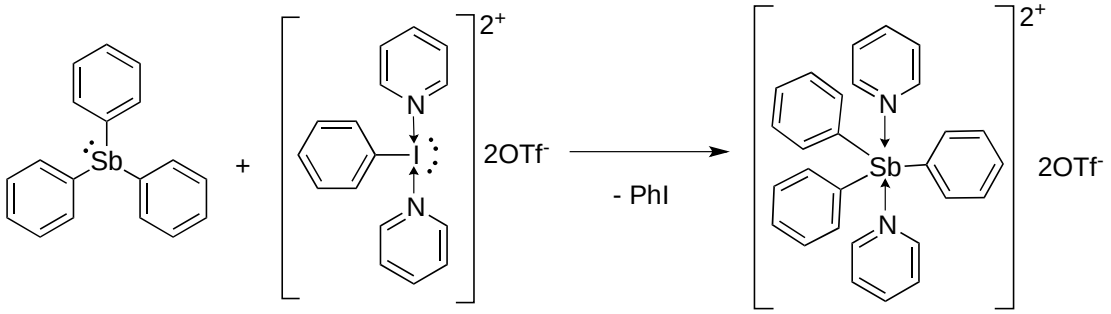


9

Scheme 7. Isolation of **9** utilizing $PhI(OAc)_2$ and attempted ligand exchange with TMS-OTf.

Antimony

The addition of $[PhI(Pyr)_2][OTf]_2$ to a CD_3CN solution of triphenylantimony did not give an immediate reaction as monitored by ^1H NMR spectroscopy. Upon overnight stirring the NMR showed the oxidant had been consumed, with PhI and a new species generated. A white powder was obtained by removing the volatiles *in vacuo*.



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Scheme 8. Oxidation of Ph_3Sb using $[PhI(Pyr)_2][OTf]_2$ yielding **10**.

Single crystals were grown from a CH_2Cl_2 solution of the isolated material via vapour diffusion into n-hexane. X-ray crystallographic studies revealed the target dicationic antimony(V) complex **10** (Scheme 8), previously reported by Burford via the multistep route outlined in Scheme 1 using 4-DMAP ligands.[3] The two pyridyl groups are coordinated axial to the central antimony with the three phenyl rings in the equatorial positions. One triflate anion with an Sb-O distance of 2.760 Å completes a distorted octahedral geometry. Overall the structure is very similar to that determined by Burford using 4-DMAP ligands.[3]

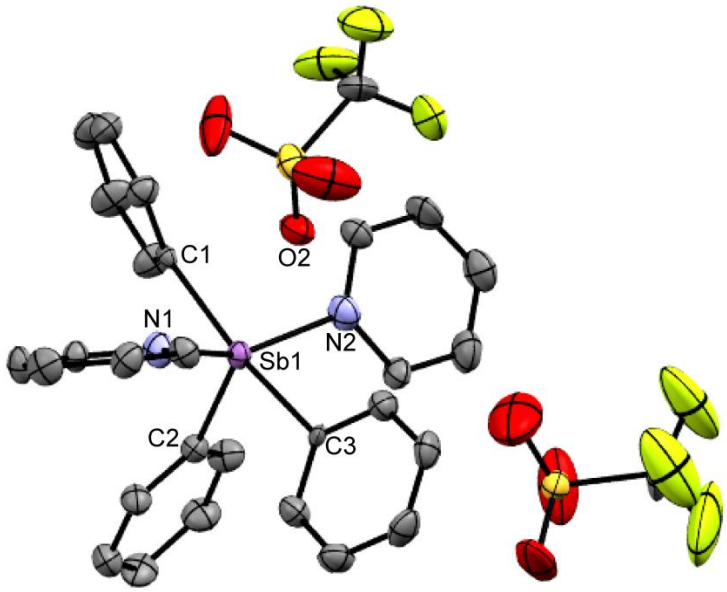
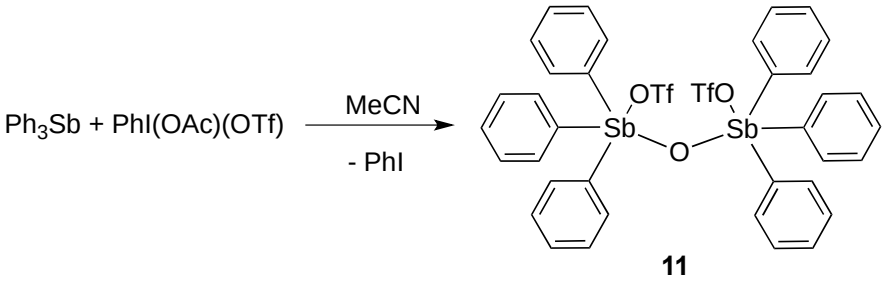


Figure 1. Solid-state structure of **10**. Chloroform and acetonitrile solvate and hydrogen atoms omitted for clarity. Thermal ellipsoids are shown at the 50% probability level. Selected bond distances (Å): Sb(1)-C(1) 2.100(4), Sb(1)-C(2) 2.124(4), Sb(1)-C(3) 2.111(4), Sb(1)-N(1) 2.272(4), Sb(1)-N(2) 2.264(4).



11

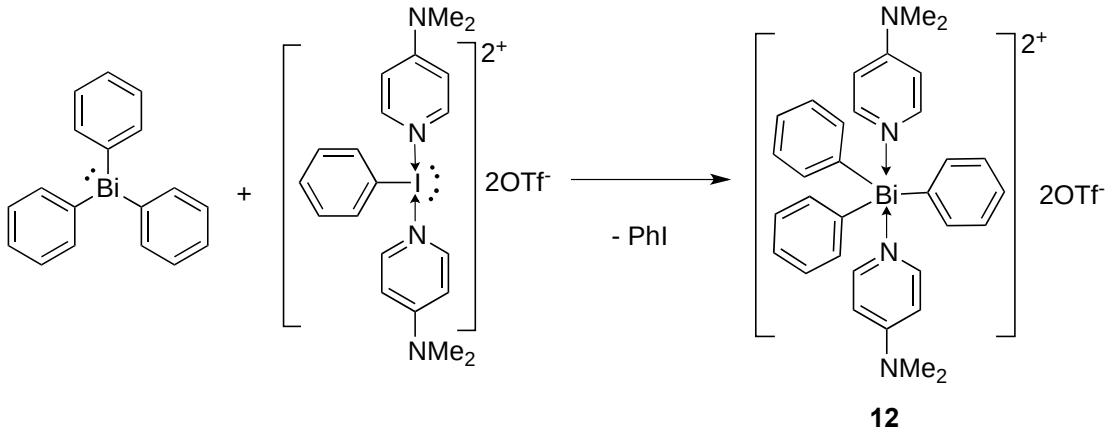
Scheme 9. The reaction of PhI(OAc)(OTf) with Ph_3Sb giving **11**.

The 1:1 reaction of Ph_3Sb and PhI(OAc)(OTf) in CD_3CN resulted in a yellow solution after stirring for 2 hours. The ^1H NMR spectrum of the reaction mixture showed a clean spectrum with the peaks associated with PhI(OAc)(OTf) being replaced with PhI, indicating an oxidation had taken place, as well as other peaks associated with phenyl fragments. Addition of n-hexane resulted in precipitation of a white powder, for which the isolated material returned a similar proton NMR to the *in situ* reaction mixture, without the PhI. A $CDCl_3$ solution of the isolated material was held at -30°C overnight yielding colorless crystals. Unit cell analysis by X-ray diffraction, then confirmed by partial refinement revealed the product to be an oxo-bridged Sb(V) species **11** with a single oxygen in the centre and each antimony capped with a triflate (Scheme 9). This compound has been previously reported and structurally characterized using a different route in which triphenylantimony oxide is reacted with triflic acid in acetone.[24, 25] This result is reminiscent of the outcome with Ph_3P with the PhI(OAc)(OTf) oxidant, in which the proposed P(V)-OTf intermediates decompose into phosphine oxide species.[17] In the case of the phosphine anhydrides could be observed in the reaction mixture, however in this case neither triflic or acetic anhydride were observed in the *in situ* reaction mixture. We do not believe the Sb-O-Sb unit arises from hydrolysis as PhI(OAc)(OTf) is highly sensitive to water (as is $[PhI(Pyr)_2][OTf]_2$) and thus rigorously anhydrous methods and solvents are used.

The reaction of Ph_3Sb with $PhI(OAc)_2$ has been previously reported to oxidize the antimony and give the expected diacetoxy Sb(V) complex.[26]

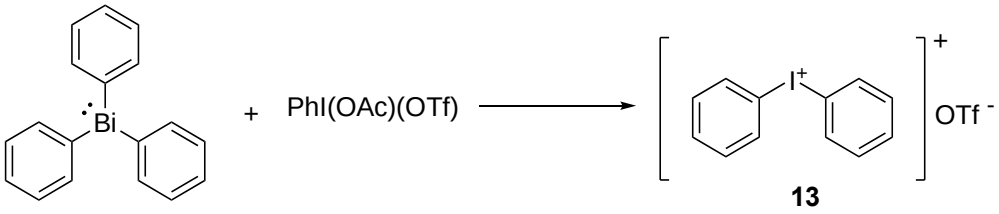
Bismuth

Ph_3Bi was added to a CD_2Cl_2 solution of $[PhI(4\text{-}DMAP)_2][OTf]_2$. CD_2Cl_2 solvent was chosen to match observations from Burford's oxidation/halide abstraction route as their NMR studies for the expected compound were done in CD_2Cl_2.[3] ^1H NMR of the solution after 2 hours showed little conversion and the mixture was left to stir overnight. After 16 hours complete conversion of the oxidant to PhI was observed, as well as one set of signals identical to that observed by Burford in CD_2Cl_2 for **12** (Scheme 10). In a bulk synthesis in CH_2Cl_2 compound **12** could be isolated in a single step with a 66% yield, an improvement over Burford's yield (41%).



Scheme 10. The reaction of $[PhI(4\text{-}DMAP)_2]^{2+}$ with Ph_3Bi giving **12**.

The addition of 1 equivalent of PhI(OAc)(OTf) to triphenylbismuth (Ph_3Bi) in chloroform resulted in an immediate change in the ^1H NMR from the 2 starting materials. Placing the solution in the freezer overnight resulted in the precipitation of colourless crystals.



Scheme 11. Addition of PhI(OAc)(OTf) to Ph_3Bi results in isolation of **13**.

X-ray diffraction studies showed via unit cell analysis[27] that the result was a diaryliodonium triflate salt **13** (Scheme 11) with ^1H NMR of the crystals also matching literature reports.[28] Compound **13** has been synthesised via numerous different methods one of which is known to involve a diarylstannane reagent.[29, 30] The proposed mechanism for the formation of these diaryliodonium salts is thought to be by a ligand exchange reaction with a nucleophilic arylating reagent containing silicon, tin or mercury.

In some experiments the *in situ* mass spectrum of the reaction mixture showed a signal that could be attributed to diphenylbismuth acetate, indicating a possible aryl exchange process giving **13** but this could not be observed reliably.

The reaction of $PhI(OAc)_2$ with Ph_3Bi is known to give the triphenylbismuth(V) diacetate.[31] As with arsenic, an attempted synthesis of a bis-triflate complex via metathesis with TMS-OTf from triphenylbismuth(V) diacetate resulted in no reaction.

Conclusion

For bismuth and antimony, use of the $[PhI(pyr)_2][OTf]_2$ class of oxidants allows for the formation of dicationic Sb(V) and Bi(V) pyridyl complexes in one step from Ph_3Pn(III) starting compounds, demonstrating the potential efficacy of this I(III) reagent in isolating high oxidation state main group compounds. However, this method was not able to access the as yet unknown As analogue. $PhI(OAc)_2$ gave the expected $Ph_3As(OAc)_2$ product when reacted with Ph_3As, complementing the already reported chemistry for Sb and Bi. The more powerful PhI(OAc)(OTf) oxidant in reactions with Ph_3Pn gave varied and generally unproductive results.

Experimental Section

All manipulations were performed under a dry N_2 atmosphere in a glovebox. Bulk solvents were dried using an Innovative Technologies Solvent Press with dual alumina columns and stored over 3 Å molecular sieves in the glovebox. NMR solvents were dried for 2 days over CaH_2, distilled and then stored in the glovebox over 3 Å molecular sieves. $PhI(OAc)_2$, TMS-OTf, pyridine, 4-DMAP, Ph_3Sb and Ph_3As were obtained from Sigma-Aldrich and used as received. Ph_3Bi, $[PhI(pyr)_2][OTf]_2$, $[PhI(4\text{-}DMAP)_2][OTf]_2$ and PhI(OAc)(OTf) were synthesized according to literature procedures.[3, 8]

Synthesis of **7**:

Ph_3As (100 mg, 0.326 mmol) was dissolved in a small amount of CD_3CN (3 mL) and added to a solution of $[PhI(pyr)_2][OTf]_2$ (215 mg, 0.326 mmol; 3 mL). The mixture was stirred for 4 hr and examined by ^1H NMR. The CD_3CN solution was left at -35°C overnight to afford large colourless crystals. Yield 34 mg 64% ^1H NMR (400 MHz, $CDCl_3$): δ 7.70 (m, 12H), 7.54 (m, 18H); $^{19}F\{^1H\}$ NMR (376 MHz, $CDCl_3$): -78.41

Synthesis of **8**:

Ph_3As (100 mg, 0.326 mmol) was dissolved in $CDCl_3$ (3 mL) and added to a solution of freshly prepared PhI(OAc)(OTf) (0.326 mmol; 3 mL). The mixture was stirred for 1 hr and examined by ^1H NMR. Colourless crystals where grown by a vapour diffusion of hexane/chloroform. ^1H NMR (400 MHz, $CDCl_3$): δ 7.82 (m, 4H), 7.73 (m, 4H), 7.64 (m, 1H); $^{19}F\{^1H\}$ NMR (376 MHz, $CDCl_3$): -78.06

Synthesis of **9**:

Ph_3As (100 mg, 0.326 mmol) was dissolved in $CDCl_3$ (3 mL) and added to a solution of $PhI(OAc)_2$ (105 mg, 0.326 mmol; 3 mL). The mixture was stirred for 24 hr and examined by ^1H NMR. The $CDCl_3$ solution was left at -35ºC overnight to afford large colourless crystals. Yield 46 mg 79%^1H NMR (400 MHz, $CDCl_3$): δ 8.05 (m, 8H), 7.51 (m, 12H), 1.72 (s, 6H).

Synthesis of **10**:

Ph_3Sb (100 mg, 0.281 mmol) was dissolved in MeCN (3 mL) and added to a solution of $[PhI(Pyr)_2][OTf]_2$ (186 mg, 0.281 mmol; 5 mL). The mixture was stirred for 1 hr and the volatiles where removed *in vacuo* leaving a white powder. Colourless crystals where grown by a vapour diffusion of hexane/CH_2Cl_2. Yield 136 mg 51 % ^1H NMR (400 MHz, $CDCl_3$): δ 8.91 (d, 4H, J = 4 Hz) 8.63 (d, 2H, J = 4 Hz), 8.03 (d, 4H, J = 4 Hz), 7.59 (t, 3H, J = 4 Hz) 7.54 (d, 6H, J = 4 Hz), 7.45 (t, 6H, J = 4Hz); $^{19}F\{^1H\}$ NMR (376 MHz, $CDCl_3$): -78.29, $^{13}C\{^1H\}$ NMR 146.4, 142.1, 134.6, 133.8, 133.2, 133.0, 130.5, 130.4, 127.6, Mp: 144-148ºC.

Synthesis of **11**:

Ph_3Sb (100 mg, 0.281 mmol) was dissolved in CD_3CN (3 mL) and added to a solution of PhI(OAc)(OTf) in CD_3CN (114 mg, 0.281 mmol; 3 mL). The mixture was stirred for 1hr and examined by ^1H NMR. The CD_3CN solution was left at -35ºC overnight to afford large colourless crystals. Yield 75 mg 53 % ^1H NMR (400 MHz, $CDCl_3$): δ 8.02 (m, 12H), 7.76 (m, 18H); $^{19}F\{^1H\}$ NMR (376 MHz, $CDCl_3$): -77.5

Synthesis of **12**:

Ph_3Bi (100 mg, 0.227 mmol) was dissolved in CH_2Cl_2 (3 mL) and added to a solution of $[PhI(DMAP)_2][OTf]_2$ (169 mg, 0.227 mmol; 3 mL). The mixture was stirred for overnight and filtered to remove unreacted oxidant. Et_2O (5 mL) was added to the solution resulting in precipitation of a colourless solid. The solution was decanted and the solid dried *in vacuo*. Yield 148 mg 66%. ^{1}H NMR (400 MHz, CD_2Cl_2): δ 7.9 (br, 4H), 7.77 (d, 8H), 7.59 (br, 7H), 6.64 (br, 2H), 3.13 (s, 12H); ^{19} F{^{1}H} NMR (376 MHz, $CDCl_3$): -78.8

Synthesis of **13**:

Ph_3Bi (100 mg, 0.227 mmol) was dissolved in $CDCl_3$ (3 mL) and added to a solution of PhI(OAc)(OTf) (114 mg, 0.227 mmol; 3 mL). The mixture was stirred for 1 hr and stored overnight at -35^{o}C. Large colourless crystals were isolated from the solution followed by removal of the solution *in vacuo*. Yield 34 mg 35% ^{1}H NMR (400 MHz, DMSO): δ 8.25 (m, 6H), 7.67 (d, 6H), 7.41 (m, 6H); ^{19} F{^{1}H} (376 MHz, DMSO): -77.74

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